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## CHLORAMINE AND CRENOTHRIX<sup>1</sup>

BY W. F. MONFORT AND O. A. BARNES

The application by Rideal of chloramine as a sterilizing agent for water and sewage has led to renewed interest in the reactions of chlorine with ammonium salts and with ammonia. Much earlier work has since been repeated in the hope of developing control of the reactions and prevention of losses. The fundamental work of Raschig has been commonly overlooked.

Chloramine (chloroamine, monochloramine) is formed<sup>2</sup> by treating dilute solutions of hypochlorites with dilute ammonia, which Raschig expresses in the following equation,  $\text{NH}_3 + \text{NaOCl} = \text{NH}_2\text{Cl} + \text{NaOH}$ .

By subjecting such a mixture to distillation in a vacuum at about 40°, after adding  $\text{ZnCl}_2$  solution to remove free ammonia and sodium hydroxide, there is obtained a concentrated solution whose analysis yields values agreeing with the formula  $\text{NH}_2\text{Cl}$ . From concentrated mixtures under greatly reduced pressure, chloramine is often obtained as pale yellow globules floating in the aqueous distillate. Because of instability in concentrated form, no attempt was made to obtain it pure. Chloramine escapes readily from its aqueous solution, has the odor of nitrogen trichloride and vigorously attacks the eyes. (C. A. 2, 1533.)

With ammonia and sodium hypochlorite in equivalent amounts (in  $\frac{1}{3}$  normal solution) there is some decomposition; liberation of nitrogen or reversion to ammonia is hastened by the presence of hydroxyl ions.

If calcium hypochlorite in equivalent amounts be substituted for sodium hypochlorite the reaction may be thus understood:



With strong solutions reacting there is here a tendency to produce nitrogen trichloride and nitrogen.

It is apparent that a solution of chloramine of only relatively low concentration can be prepared; that if stronger solutions of bleach

<sup>1</sup> Read before the Illinois Section, March 25, 1919.

<sup>2</sup> Raschig, 1907, Chem. Zeit., 31, 926.

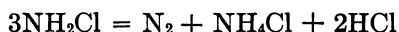
and of ammonia are used, the reaction must take place in the presence of considerable amounts of diluting water.

Experiments were undertaken to determine the stability of chloramine solutions of different strengths. There are two methods of determining the velocity of the reaction: (1) the content of chloramine remaining in the solution after the lapse of each period of test, and (2) the total volume of nitrogen evolved in a gas burette at the end of each period. The results of the experiments are given in table 1.

TABLE 1  
*Decrease in available chlorine of a chloroamine solution*

HOURS	CHLORINE	NITROGEN EVOLVED FROM 50 CC. SOLUTION	HOURS	CHLORINE	NITROGEN EVOLVED FROM 50 CC. SOLUTION
	<i>p.p.m.</i>	<i>cc.</i>		<i>p.p.m.</i>	<i>cc.</i>
0	1003.443	0	23	860.09	
1	1003.443	0	24	850.00	0.51
2	1003.443	0	25	850.84	
3	1003.443	0	26		0.63
4	984.68	0.01	28		0.69
5	980.86	0.05	29	841.28	
6		0.09	32		0.73
7	975.12	0.12	51	707.44	
8		0.15	54		1.6
8½	965.56		73	554.48	
10		0.17	76		2.5
11½		0.27	98	430.20	
17	889.08		101		3.25
19	879.52		145	296.36	
20		0.37	148		4.10
21	869.96		170	213.00	
22		0.44	173		4.50

The amount of nitrogen evolved is a function of the rate of disappearance of available chlorine, which finds expression in the equation:



A series of determinations was made of the rate of decomposition of chloramine solutions of different strengths, as given in table 2.

The most concentrated solution used (10.2 grains available chlorine per liter, or 0.2877 normal) foamed vigorously at the start; the succeeding one less, and so through the several series, with the velocity

of the decomposition diminishing in each case as the period of experiment was prolonged, as indicated both by the volume of gas evolved and the concentration of available chlorine. A precipitation of cal-

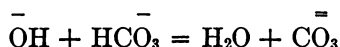
TABLE 2  
*Decomposition of chloroamine solutions*

HOURS	SERIES	AVAILABLE CHLORINE		HOURS	SERIES	AVAILABLE CHLORINE	
		Parts per million	Loss			Parts per million	Loss
0	1	10200	0	0	2	8160	0
1	1	7275	28.68	1	2	7388	9.46
2	1	6900	32.35	2	2	7013	14.06
3	1	6413	37.13	3	2	6619	18.88
7	1	4875	52.26	7	2	5438	33.36
11	1	3844	82.90	11	2	2194	45.76
24	1	1744	82.90	24	2	2194	73.11
32½	1	1125	88.97	32½	2	1819	77.71
53½	1	300	97.06	53½	2	469	93.03
0	3	6120	0	0	4	4080	0
1	3	5513	9.92	1	4	3750	8.09
2	3	5250	14.21	2	4	3638	10.83
3	3	4988	18.50	3	4	3516	13.82
7	3	4350	28.92	7	4	3169	22.33
11	3	3788	38.10	11	4	2897	29.00
24	3	2175	64.46	24	4	2016	50.59
32½	3	1538	74.87	32½	4	1603	60.71
53½	3	563	90.80	53½	4	863	78.85
0	5	3060	0	0	6	2040	0
1	5	2775	9.31	1	6	1875	8.09
2	5	2700	11.76	2	6	1844	9.61
3	5	2625	14.22	3	6	1813	11.13
7	5	2391	21.86	7	6	1706	16.37
11	5	2231	27.09	11	6	1638	19.71
24	5	1688	44.84	24	6	1350	33.82
32½	5	1397	54.35	32½	6	1194	41.47
53½	5	853	72.12	53½	6	863	57.69

cium hydroxide varied in the series of reactions from very heavy in the first to relatively slight in the last.

From these data it is apparent why the application of chloramine should be made under such conditions that the concentration of the mixed reagents shall not exceed 1 p.p.m. A solution even of this

low concentration should not be stored longer than twenty-four hours and is best made up as used. Not only do hydroxyl ions in solutions prepared from bleach and ammonia reduce the stability of chloramine; their reactions with bicarbonate ions in the treated water convert the latter to bivalent carbonate ions, and cause a copious precipitation of calcium carbonate.



This has resulted in incrustation of feed pipes and of lines carrying the treated water from the point of applying chloramine.

Some experiments were carried on in preparing chloramine with dilute chlorine water and dilute ammonium compounds,  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{CO}_3$ , etc., with varying results. While it is theoretically possible that some chloramine might be formed under these conditions, the diverse possibilities of reaction, indicated by Bray and Dowell<sup>3</sup> offer little hope that direct addition of ammonia and liquid chlorine to a water can be so controlled and the distribution of the sterilizing agent be made so efficient as to insure the full chlorine equivalent in chloramine.

Rideal<sup>4</sup> found that when chlorine was introduced into sewage it was rapidly consumed, but that after free chlorine had entirely disappeared there persisted a strong germicidal power. The same results were obtained when bleaching powder was added to a water containing a small amount of ammonia. It seemed probable that the ammonia did not increase the oxidizing power of chlorine, since readily oxidizable organic matter in water absorbed much less chlorine from ammonia and hypochlorite than from hypochlorite alone. Furthermore the bleaching effect on dyestuffs indicated that ammonia and bleach together had only two per cent of the oxidizing (bleaching) power of hypochlorite alone. While chloroamine has little oxidizing value it is still able to displace iodine from potassium iodide, giving the usual starch-iodide reaction; its chlorine can be precipitated by silver nitrate, and its ammonia equivalent determined with the strongly alkaline Nessler's reagent. Rideal showed that chloroamine has a phenol coefficient of 6.6, three times that of chlorine.

According to Dakin<sup>5</sup> the germicidal value of hypochlorite in

<sup>3</sup> Bray and Dowell, *J. Am. Chem. Soc.*, 39, 905.

<sup>4</sup> Rideal, *J., Roy. San. Inst.*, 31, 33, 1910.

<sup>5</sup> Dakin, *Proc. Roy. Soc. Lond., Series B.* 89, B. 614, pp. 232-251.

sewage is due to chloroamine derivatives produced by the action of chlorine on amino acids and proteins. The proteins present in sewage contain amino groups which may react with chlorine to form substituted chloramines containing the NCl group. When chlorine or bleaching powder is added to sewage, there may occur a primary oxidation and a secondary formation of toxic chloramines from the reaction of aminobodies. When chloroamine is added to sewage the initial rapid oxidation is eliminated, and the germicidal action begins at once. Dakin attributes the latter action to the chloramine group.

It is possible that proteins of living cells may so react, and that the killing of microorganisms by hypochlorites is due to chemical changes of this character within the living cell, either by direct action of the germicide or by secondary products of similar nature.

*Action of chloroamine on crenothrix.* The pronounced success of chloramine treatment in the destruction of vegetative bacterial cells suggested its application to an especially troublesome water pest. *Crenothrix* is one of the iron bacteria, so called, because of their occurrence in iron-bearing waters. It belongs with the true bacteria (eubacteria). Its cylindrical cells are united in unbranched threads, enlarged toward the free end, covered with a thick sheath which becomes infiltrated with ferric hydroxide. Reproduction takes place by the division of the cells in three planes, with the formation of round gonidia. It is still in dispute whether the organism receives its energy from oxidation of ferrous to ferric iron<sup>6</sup> or whether the separation of ferric hydroxide is an independent mechanical phenomenon not connected with the life processes of the cell.<sup>7</sup>

It occurs in numerous sections of the State of Illinois in surface waters and in some well supplies, as at Freeport and Champaign-Urbana. In 1917 the latter supply was rendered unsightly and unfit for some domestic purposes by the development and decay of the organisms in the distribution system.

In carrying on the experiments upon the action of chloroamine on *crenothrix* it was impossible to plate the treated water on media, as is done with ordinary water bacteria, since no medium had been discovered upon which it can be surely grown.

Chloroamine was first tried on water from the University well, which furnishes an iron-bearing water already inoculated with

<sup>6</sup> Winogradsky, Proc. Zool. Soc. Lond., 1913, Pt. 2, 430.

<sup>7</sup> Mollisch and Ellis.

crenothrix. The first tests demonstrated in duplicate 800 cc. samples the germicidal action of 1 p.p.m. available chlorine in freshly prepared chloramine. At the end of a week there was no growth in the treated samples, while control samples, untreated, showed an abundant reddish growth on the bottom.

In later series 11-liter samples were used: one set with chloroamine in amounts equivalent to 0.5, 0.75 and 1 p.p.m.; a second with bleaching powder equivalent to 1 p.p.m. available chlorine. Control samples stored without treatment showed an abundant growth at the end of one week. At the end of three weeks water treated with bleach alone showed a velvet growth, identified as crenothrix by microscopical examination. Samples treated with 1, 0.75, and 0.5 p.p.m. of available chlorine in chloramine gave no growth at this time nor within six months thereafter. The odor in the last mentioned samples was pleasant, noticeably better than that of untreated or bleach-treated samples; nor was there at any time a noticeable taste, save in those which had received the largest application of chloroamine (1 p.p.m.), in which there was a slight flavor as of chloroamine. In the controls and in the bleach-treated waters, the taste and odor were offensive.

These tests were repeated with similar results. A chloroamine addition corresponding to 0.5 p.p.m. was effective in preventing development of crenothrix; the residual matter did not become offensive even after prolonged storage.

These results, gotten in a small way, indicated that the acute troubles arising from crenothrix in iron-bearing waters may be eliminated by the germicidal action of chloroamine, thus reducing the problem of treatment to one of iron removal without complications. It was intended to apply the experiment in a large way at the 2,000-000-gallon plant of the Champaign-Urbana Water Company immediately after the conclusion of the first experiments. There was at the time (January, 1918) difficulty in commanding a supply of ammonia and of reliable bleaching powder. The method substituted, the use of liquid chlorine, is described on page 194.